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MECHANISM OF HYDROCRACKING

Reactions of Paraffins and Olefins

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Reactions of paraffins and olefins during hydrocracking have been studied. The types of reactions are shown to depend to a major extent on the activity of the hydrogenation component in dual-function catalysts. The almost exclusive reaction noted previously with hydrocracking catalysts under representative hydrocracking conditions was extensive splitting, primarily to low molecular weight paraffins (C_8-C_6). In direct contrast, a catalyst with very high hydrogenation activity gave products not noted previously: isomerized uncracked paraffins, higher molecular weight cracked paraffins characteristic of primary rather than secondary cracking, and cyclics. A mechanism is presented to predict and explain contrasting reactions and products from different types of catalysts.

THE LARGEST catalytic operation of the petroleum industry, and of all industry as well, is the conversion of heavy petroleum stocks to gasoline and light domestic burner fuels. The total current capacity in the United States alone is about 5 million barrels per day. With such a tremendous operation, even small improvements are of major economic significance.

An alternate process, hydrocracking—that is cracking under hydrogen pressure, is under intensive study by many companies. Changes in refinery operations and the development of new catalysts and techniques have raised the potential of this mode of operation.

One of the hydrocracking catalysts with exceptionally good activity and selectivity is comprised of platinum on a solid mixed oxide of high activity (4). This dual-function catalyst combines both high hydrogenation and acid activities. The higher selectivities and changes in product distribution found for this catalyst, indicated that the hydrocracking reactions might differ appreciably from those conventionally obtained. Consequently, reactions of pure compounds have been studied further to determine hydrogenation and acid activity requirements for maximizing and minimizing certain hydrocracking reactions. These studies also have led to new concepts on the mechanism of hydrocracking.

Prior Studies on Hydrocracking Reactions

The reactions of paraffins over various hydrocracking catalysts have been studied previously by several authors. The principal reaction noted was extensive splitting to low molecular weight paraffins, C_8-C_6 predominantly. Other products were small or negligible; the uncracked paraffin was not isomerized.

These reactions contrast with those observed with dual-function catalysts under hydroreforming conditions at generally higher temperatures and lower pressures. In such cases the normal C_8-C_6 paraffins studied were partially aromatized and extensively isomerized (3, 10, 13-15). Mills, Heinemann, Milliken, and Oblad (16) investigated reforming catalysts and proposed a mechanism involving: formation of an olefin on a hydrogenation site, isomerization on an acid site, and saturation on a hydrogenation site. It has been shown by Weisz and Swegler (22) that such intermediates can and most likely do move in the gas phase between the two sites.

Hydrocracking studies were made by Pier (18) using tungsten sulfide. He concluded that paraffins were isomerized and split on the carbon atom with the least hydrogen and that representative paraffins could not be isomerized without simultaneous splitting. Flinn, Larson, and Beuther (6) studied reactions of octane and hexadecane over nickel-silica-alumina under hydrocracking conditions. Products were predominantly light, extensively isomerized paraffins from cracking, but the *n*-paraffin charge was not isomerized. They proposed a mechanism combining rapid isomerization with cracking and a tendency for hydrogenation of branched olefins formed by cracking.

Archibald, Greensfelder, Holzman, and Rowe (7) found that under hydrocracking conditions tungsten sulfide on silica-alumina or fluorided Filtral converted paraffins (C_7 through C_{16}) primarily to light paraffins (generally C_8-C_6) and also reported that no straightforward isomerization of any paraffinic feedstock to any of its isomers was observed. They also concluded that isomerization takes place only with cracking and that hydrocracking of aliphatics follows the carbonium ion mechanism of catalytic cracking with hydrogenation superimposed. Thus, there are marked differences in both types of products and mechanisms that have been proposed for hydroreforming and hydrocracking.

Experimental

Catalysts. Platinum-silica-alumina was prepared using a silica-alumina with 10 wt. % alumina and a surface area of 420 square meters per gram. The support was crushed and screened to 10-25 mesh (U. S. Standard). The final catalyst had 0.5 wt. % platinum which was added by vacuum impregnation with chloroplatinic acid by procedures described previously (4).

Molybdena-silica-alumina was prepared from the same silica-alumina. The final catalyst had 10.5 wt. % of molybdena which was added by vacuum impregnation with an oxalic acid solution of ammonium molybdate (85% molybdcic acid). After impregnation, the catalyst was heated for 16 hours at 110° C. in a covered beaker and then calcined in air for 16 hours at 538° C.

Cobalt-molybdena-silica-alumina was pelleted to 1.6 × 3.2 mm. particles. The catalyst had 2.7 wt. % cobalt oxide, 7.9 wt. % molybdena, 73.2 wt. % alumina, and 15.1 wt. % silica. Surface area was 238 square meters per gram.

Charge Stocks. *n*-Heptane (Phillips Petroleum Co. pure grade) was indicated to be 99.9% pure by mass spectroscopy. *n*-Hexadecane (Humphrey-Wilkinson) was indicated to be 99.8% pure by mass spectroscopy. *n*-Docosane (Humphrey-Wilkinson) had a specific gravity 15.56°/15.56° C. = 0.7999; $N_D^{\circ} = 1.4268$. 1-Hexadecene (Humphrey-Wilkinson) had a minimum purity of 95% indicated by the supplier; specific gravity 15.56°/15.56° C. = 0.7844; $N_D^{\circ} = 1.4421$. 17-Pentatriacontene (Armour & Co.) contained substantial amounts of C_{11} and C_{13} compounds and some material that was not straight chain; $N_D^{\circ} = 1.4421$.

Procedures and Analyses. A continuous flow unit described in a prior article (4) was used. The reactor held 100 cc. of catalyst.

Reaction conditions were: 1000 p.s.i.g., 0.5 liquid hourly space velocity, and a hydrogen rate of 3.185 liter (STP) per ml. of charge (at 15.56° C.). The catalyst was brought to an equilibrium condition (4) by charging a light paraffin wax or a light gas oil for several days. When a stable state was reached, the pure hydrocarbon was charged. The conversion level was regulated by temperature. Material balances were made when a stable state was attained after several hours on stream with the pure hydrocarbon, except for two hexadecane experiments with the platinum catalyst (53 and 98% conversion) where the prerun with hexadecane was only 1.5 hours. The procedure was repeated with each charge stock.

Analyses of gases were made as described previously (4). The liquid products were distilled in a Podbielnik column to 52° C. The residues were fractionated in a micro-Podbielnik column (50 to 60 theoretical plates). Cut points in each case were 81°, 88°, 101°, 104°, and 111° C. The carbon number of the naphthenes above C_7 was estimated from the naphthene content of individual fractions boiling between 111° and 199° C. The uncracked C_{18} (with hexadecane and hexadecene charge) was calculated as material boiling above 260° C. (There was no product above C_{16} . The C_{11} product must have been very small, since it must correspond with methane formation at a maximum. The C_{14} paraffins and naphthenes were also indicated to be small from ethane analyses, and, moreover, essentially all boiled below 260° C.).

The fractions were analyzed by mass spectroscopy using matrices developed in these laboratories. The amount of paraffin of a specific carbon number was estimated assuming a constant iso to normal ratio for the C_{8+} paraffin products. The average degree of branching (isomerization) of the unconverted C_{15} and C_{22} was determined by infrared analysis (7).

Terminology. Conversion and cracking are used interchangeably to designate the weight per cent of charge converted to products with carbon number differing from that of the charge. It does not include conversion to cyclo- or

Table I. Effect of Conversion Level on Product Distribution when Hydrocracking Hexadecane over a Platinum Catalyst

Products	Moles/100 Moles Cracked			
	53.1% conv., 371° C. ^a	81.6% conv., 370° C.	98.0% conv., 394° C.	(100)% conv., 394° C.
Paraffins				
C_1	1	1	1	2
C_2	1	1	1	1
C_3	7	8	10	23
C_4	19	21	32	62
C_5	21	23	37	55
C_6	17	17	32	36
C_7	22	23	38	33
C_8	24	29	30	26
C_9	22	22	21	13
C_{10}	19	15	12	7
C_{11}	18	13	7	4
C_{12}	13	14	3	1
C_{13}	3	4	1	0
C_{14}	1	1	1	0
C_{15}	1	0	0	0
Total paraffins	189	192	226	263
Naphthenes	14	16	12	13
Total	203	208	238	276

^a Hexadecane charged only 1.5 hr. prior to material balance. Catalyst was not at equilibrium temperature.

isomers of the same carbon number as the charge. Moles per 100 moles cracked refers to moles of products per 100 moles converted to products of different carbon number.

Results

Hexadecane Hydrocracking at Different Conversion Levels. Hexadecane was hydrocracked over the platinum catalyst at four conversion levels: 53, 82, and 98% and at a temperature more severe than required for 100% conversion. The products are shown as moles of specific carbon number product per 100 moles of hexadecane cracked in Table I. These results are shown graphically in Figure 1 where products are shown as per cent of carbon atoms in the converted charge (rather than mole distribution). Hexadecane split fastest at the C_8 bond and at progressively lower rates at bonds more

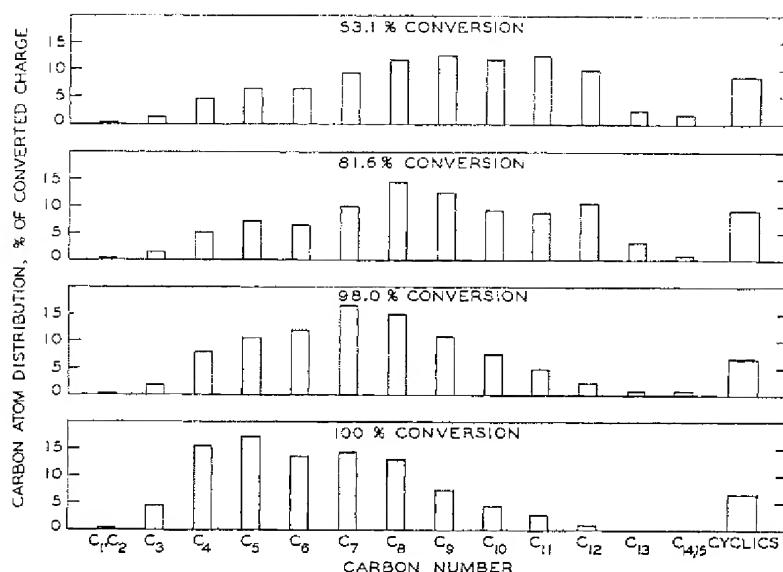


Figure 1. Hexadecane hydrocracking over catalyst with high hydrogenation activity (platinum)

distant. Composition was quite constant until conversion reached about 100%; only then did any appreciable secondary splitting occur. The extent of cyclization is shown in Table II. Isomerization of the light products and of the unconverted charge is listed in Table III.

The products with this type of catalyst are strikingly similar until conversion reaches about 100%:

There is very little secondary splitting (only slightly more than 200 moles of product per 100 moles cracked).

Products are primarily C_4 - C_{12} .

Splitting to C_7 , C_8 , and C_9 predominates.

Only at high conversions (about 98% and higher) does secondary splitting occur. Even at these high conversions, there are marked similarities in products with those at lower conversion levels:

Cyclization primarily to naphthenes gives 12 to 16 moles per 100 moles cracked.

Polymerization to products of higher molecular weight is negligible.

The degree of isomerization of the C_4 , C_5 , and C_6 paraffins is quite constant.

Reactions of Paraffins of Differing Molecular Weight. The same types of reactions were observed with *n*-heptane and *n*-docosane (Table IV) as with *n*-hexadecane. Secondary cracking is small in all cases but appears to increase to some extent with molecular weight. Thus, *n*-docosane gives somewhat more secondary cracking at a 94% conversion than *n*-hexadecane at 98%. Cyclization was very small with *n*-heptane relative to the higher molecular weight charge stocks. Isomerization of the uncracked heptane increased with conversion and reaction severity (Table V) and was extensive even at low conversions. The uncracked hexadecane and docosane were also very highly isomerized, with an average degree of branching being somewhat higher with the former (approximately two branches per molecule *vs.* 1.2 with docosane).

Table II. Cyclization in Hexadecane Hydrocracking

Products	Moles/100 Moles Cracked ^a			
	53.1% conv.	81.6% conv.	98.0% conv.	(100)% conv.
Naphthenes				
C_5	1.0	1.0	0.2	0.3
C_6	0.3	0.4	1.0	1.5
C_7	0.8	1.3	2.6	3.4
C_{8+}	11.7	13.2	8.2	7.6
Dicyclic	...	0.1	0.2	0.5
Aromatics				
Monocyclic	0.3	0.3	0.3	0.2
Naphthalene aromatics	Tr	0.1
Dicyclic	Tr	Tr
$C_6H_{10-14-2n-18}$	Tr
$C_7H_{14-18-2n-22}$	Tr
C_8H_{2n-22}	Tr	Tr ^b

^a Tr = trace.

^b Pyrene in product was 0.02 wt. % of charge (by ultraviolet analysis).

Table III. Isomerization in Hexadecane Hydrocracking

Conversion, %	<5	53.1	81.6	98.0	(100)
Isoparaffin, wt. % of normal + isoparaffin					
C_4	...	59	58	54	56
C_5	...	70	67	65	68
C_6	...	62	64	67	65
Av. No. of branches per molecule		1.1	1.9	2.1	...
C_{16}					

Table IV. Hydrocracking of Paraffins and Olefins over Platinum Catalyst

Products	Moles/100 Moles Cracked ^a				
	<i>n</i> - Heptane 49.5% conv., 471° C.	<i>n</i> -Docosane 33.5% conv., 310° C.	1-Hexadecene 94.3% conv., 336° C.	7-Penta- triacontene 67.1% conv., 348° C.	
	471° C.	310° C.	336° C.	348° C.	
Paraffins					
C_1	9	<1	<1	1	<1
C_2	6	1	2	<1	1
C_3	95	4	11	9	16
C_4	82	9	31	21	49
C_5	5	9	31	21	49
C_6	5	6	25	15	15
C_7	...	12	27	22	23
C_8	...	13	27	26	43
C_9	...	16	23	22	44
C_{10}	...	9	20	17	32
C_{11}	...	7	16	15	24
C_{12}	...	11	12	17	25
C_{13}	...			5	21
C_{14}	...			2	13
C_{15}	...	83	33	1	7
C_{16}	3
C_{17+}	11
Total paraffins	202	180	258	194	376
Naphthenes					
C_5	2	0.3	0.5	0.3	0.4
C_6	Tr	0.1	0.8	0.2	0.6
C_7	...	<1	1.0	0.9	2.6
C_8	...	0.8	1.2		
C_9	...	1.3	2.3		
C_{10}	...	0.7	2.2	5.6	30.0
C_{11}	...	1.0	1.9		
C_{12+}	...	5.7	2.5	1.7	
Dicyclic	...	<1	0.2	0.2	0.6
Total naphthenes	2	10	13	9	34
Aromatics					
Aromatics	Tr	0.1	0.1	0.1	0.4
Total	204	190	271	203	411

^a Tr = trace.

Reactions of Olefins. Hexadecene gave products very similar to those obtained from hexadecane when hydrocracking over the same platinum catalyst (Table IV). The penta-triacontene underwent extensive secondary cracking at the test condition used. However, even in this case (411 moles of products per 100 moles cracked), there were relatively small amounts of C_5 - C_6 , amounting to only 18 wt. % of the charge. The products were predominantly C_8 and higher boiling products.

Hydrocracking Hexadecane with Mo- and Co-Mo-Silica-Alumina. Hexadecane was hydrocracked at 30 to 35% conversion levels over molybdena-silica-alumina and cobalt-molybdena-silica-alumina. Even at these low levels, there was a small amount of secondary splitting with the molybdena catalyst but none with the cobalt-molybdena catalyst (Table VI). Cyclization was less than half that obtained with the platinum catalyst. The degree of isomerization of the unconverted charge was platinum > cobalt molybdate > molybdena.

Hydrogenation Activity. The relative hydrogenation activities of the three catalysts were indicated to be platinum > cobalt molybdate > molybdena. There is no entirely suitable quantitative test of activity, since test conditions and hydrocracking conditions differ. One type of test developed by Eastwood, Wantuck, and Kelly of these laboratories used a charge of benzene (containing 1 wt. % thiophene with the nonplatinum catalysts) at 1000 p.s.i.g., 2 liquid hourly space velocity, and 10 moles of hydrogen per mole of charge at 371° C.

The per cent of benzene hydrogenated served as a measure of hydrogenation activity. In this test, platinum catalysts had a value of 100; a sulfided cobalt-molybdena-silica-alumina, 22; and a molybdena catalyst on an acidic base (not silica-alumina), a value of 14. Another type of test developed by the authors and Miale of these laboratories measured the relative hydrogen activity when hydrocracking a light gas oil at 1000 p.s.i.g., 0.5 liquid hourly space velocity, using 3.185 liter (STP) of hydrogen per ml. of charge (at 15.56° C.). The degree of saturation of monocyclics in the 77° to 199° C. naphtha was related to an empirical value:

$$f_R = 100 \left\{ 1 - 2 \left[100 \left(\frac{A}{A+N} \right) - \left(10^{aR^2} + bR + c + 0.5 \right) \right] \right\}$$

where A and N are the weight percentages of monocyclic aromatics and naphthenes, R equals $1000/T$ (° F.), and con-

Table V. Isomerization of *n*-Heptane during Hydrocracking

	<1	4	49.5
Temp., ° C.	327	369	411
Heptane isomerization, %	11.1	60.8	88.9
	% of C ₇ Paraffins		
<i>n</i> -Heptane	88.9	39.2	11.1
2-Methylhexane	4.6	23.4	30.3
3-Methylhexane	5.1	32.2	57.7
2,2-, 2,3-, and 2,4-dimethylpentanes	0.3	3.5	0.9
3-Ethylpentane	0.6	0.3	...

* To products of other than seven carbon atoms.

Table VI. Hydrocracking Hexadecane over Molybdena-Silica-Alumina and Cobalt-Molybdena-Silica-Alumina

Products	Moles/100 Moles Cracked		
	Molybdena-Silica-Alumina	Cobalt-Molybdena-Silica-Alumina	
		30.4% conv., 375° C.	34.3% conv., 375° C.
Paraffins			
C ₁	...	2	
C ₂	1	1	
C ₃	17	8	
C ₄	34	22	
C ₅	31	21	
C ₆	21	13	
C ₇	25	19	
C ₈	23	26	
C ₉	16	21	
C ₁₀	13	17	
C ₁₁	10	13	
C ₁₂₊	26	32	
Total paraffins	217	195	
Naphthenes			
C ₆	0.4	0.4	
C ₇	0.1	0.2	
C ₈	1.3	0.7	
C ₈₊	4.5	4.9	
Total naphthenes	6	6	
Total moles	223	201	
Av. No. of branches per C ₁₀ molecule	0.9 ^a	1.5 ^b	

^a 0.4 branch per molecule at <5% conversion, 353° C. ^b 0.7 branch per molecule at <5% conversion, 352° C.

Table VII. Effect of Hydrogenation Component on Types of Paraffin Hydrocracking Reactions

Platinum Catalyst	Nickel or Tungsten Sulfide Catalyst
Primary splitting to give two intermediate size paraffins	Secondary splitting extensive, mainly to C ₄ -C ₆ paraffins
Isomerization of paraffin charge	No isomerization of charge detected
Cyclization principally to naphthenes	Cyclic formation small or not noted

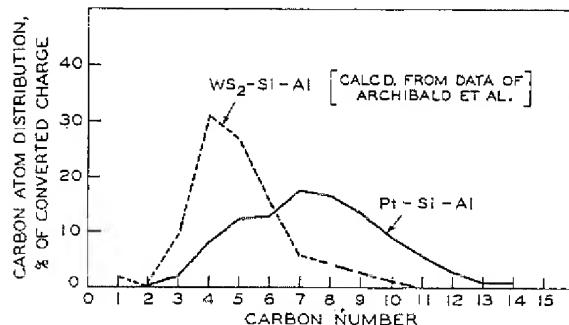


Figure 2. Effect of catalyst hydrogenation activity on product distribution in hydrocracking

Comparisons made at 81% conversion with each catalyst

stants a , b , c = -33.8, 80.79, -46.93. Values for platinum, cobalt-molybdena, and molybdena catalysts were 100, 52, and 42, respectively. In both tests, 100 indicates equilibrium was attained; thus, a hydrogenation activity of 100 may be much greater than would be indicated by a direct ratio comparison with catalysts having values below 100.

Discussion

Catalysts with Different Hydrogenation Components. From a practical point of view, the reactions most desired in hydrocracking of paraffinic constituents are: isomerization of the charge, formation of cyclics, and controlled (primary) splitting to molecules of desired size without secondary splitting to light paraffins. These are the reactions found with a highly active hydrogenation component—platinum—over almost the entire conversion range to 100%. By contrast, less active hydrogenation components, tungsten sulfide and nickel at conversions of 62 to 99% and 95 to 99%, respectively (1, 6), produced no isomers of the charge and extensive secondary cracking (Table VII). The marked difference in products between platinum-silica-alumina and tungsten sulfide-silica-alumina at 81 to 82% conversion levels is shown in Figure 2.

The tests with the molybdena and cobalt-molybdena catalysts were at relatively low conversion levels (30 to 35%). Under these conditions, the same types of reactions were observed as with platinum catalysts. However, the charge was less isomerized and cyclic formation was lower. Moreover, secondary splitting was as extensive at 30% conversion over the molybdena catalyst as it was at about 90% conversion over the platinum catalyst.

Catalyst Cracking vs. Hydrocracking Reactions. The term catalytic cracking is used in this work to refer to the well-known cracking of hydrocarbons over acidic catalysts (e.g., silica-alumina) in the absence of any added hydrogen and generally at pressures only slightly above atmospheric. The reactions of hexadecane have been studied quite extensively (5, 8, 11, 12). A comprehensive study of catalytic cracking of decane was made by Plank, Sibbett, and Smith (79).

The marked differences in products obtained from hexadecane by catalytic cracking and by hydrocracking over platinum-silica-alumina are summarized in Table VIII. All classes of products—paraffins, olefins, naphthenes, aromatics, polymers, coke—differ appreciably in structure and radically in quantity.

Furthermore, there are marked similarities in catalytic cracking with different catalysts and conditions. Secondary

Table VIII. Comparison of Products from *n*-Hexadecane

Products	Hydrocracking Over Pt/Si/Al	Catalytic Cracking (5, 8, 11, 12, 20)
Paraffins	C_4 through C_{12} predominant; lesser amounts of C_8 and C_{10} ; negligible C_1 , C_2 , C_{14} , C_{16} . C_{16} isomerized	C_8 through C_{16} predominant; small amount $>C_{16}$; appreciable C_1 and C_2 ; C_{16} not isomerized
Olefins	Negligible	Substantial; C_2 - C_6 predominant; C_8 and C_{10} may be 50-60% olefin; per cent olefin increases with reaction temperature
Naphthenes	12 to 16 moles formed per 100 moles cracked; C_8 through C_{12} predominant	Not reported; apparently very small
Aromatics	Very small amount; monocyclics in thermodynamic equilibrium with naphthenes	Present (amount not specified); C_8 through C_{11} predominant; aromatics with carbon number greater than C_{15}
Coke	Negligible	Formed 1 wt. % at 40% conversion

cracking is extensive (about 350 moles per 100 moles cracked) and nearly constant from conversions as low as 11% up to 68% conversion (12). Liquid recycle and different reaction conditions do not have a major effect on product distribution. Some catalysts (e.g., silica-magnesia) (8) give slightly more C_{6+} product, but the major reactions still involve extensive secondary splitting to give primarily C_8 - C_{10} from all higher paraffins.

The marked differences in product distribution by catalytic cracking and by platinum hydrocracking of hexadecane are shown in Figure 3. However, product distribution was quite similar to that obtained when hexadecene is catalytically cracked. Comparisons were made at 53% conversion in both cases. Nickel or tungsten sulfide hydrocracking (1, 6) gave product distributions much closer to that of catalytic cracking than platinum hydrocracking.

Mechanism of Hydrocracking

The mechanism presented here is an adaptation of that proposed by Mills, Heinemann, Milliken, and Oblad for dual-

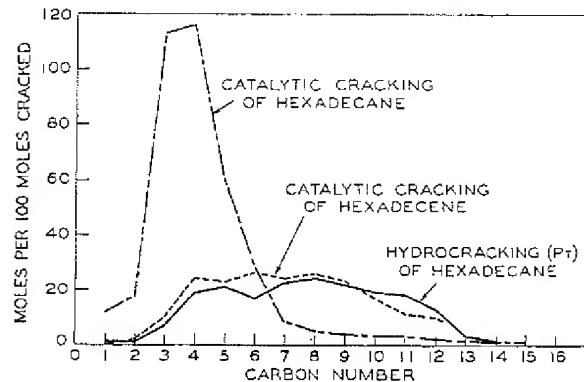


Figure 3. Product distribution when hydrocracking hexadecane and catalytic cracking hexadecane and hexadecene

Comparisons made at 53% conversion

function reforming catalysts. Concepts on the mechanism of hydrocracking postulating that isomerization occurs and splitting follows immediately, or that hydrocracking is catalytic cracking with hydrogenation superimposed, do not adequately describe the mechanism.

The mechanism presented here is extended to account for the wide difference in types of products reported for reforming and for hydrocracking. In addition, the mechanism accounts for the wide difference between the types of hydrocracked products reported here and those in the earlier literature. These include major differences in isomerization of uncracked charge, an opposite effect on the iso to normal ratio in cracked products, degree of secondary cracking, and cyclization. These are related to relative reaction rates over hydrogenation and acidic sites.

Evidence for Olefinic Intermediates. Evidence for an olefinic intermediate in hydrocracking is the similarity in product distribution from:

Hydrocracking of a paraffin (hexadecane) over platinum-silica-alumina.

Catalytic cracking of an olefin (hexadecene) over an acidic catalyst devoid of hydrogenation component.

Data are summarized in Table IX for these two entirely different systems at two identical conversion levels, 53 and 83%. There was a remarkable similarity in carbon number of the products at 53% conversion levels (Figure 3). Also, secondary cracking was very small, and extensive isomerization of the C_{16} charge occurred in both cases.

In contrast, catalytic cracking of a paraffin, hexadecane, at the same (53%) conversion level gave an entirely different product distribution from that obtained with the olefin (Table IX and Figure 3). Some emphasis has been placed in the past on the similarity of products from catalytic cracking of a paraffin and an olefin charge (9, 20). However, it rather appears more desirable to stress the marked dissimilarities—especially at moderate conversions.

It is true that more secondary splitting occurs in catalytic cracking of the hexadecene at a higher conversion level (83%)

Table IX. Comparison of Products from Hydrocracking and Catalytic Cracking

Products	Moles/100 Moles Cracked				
	Hydro-cracking ^a	Catalytic Cracking ^b	Catalytic Cracking ^c	Hydro-cracking ^a	Catalytic Cracking ^b
	Hexadecane charge, 53.1% conv.	Hexadecene charge, 53.3% conv.	Hexadecane charge, 53.5% conv.	Hexadecane charge, 81.6% conv.	Hexadecene charge, 81.6% conv.
Carbon no.					
1	1	0	12	1	0
2	1	2	18	1	0
3	7	10	113	8	27
4	19	24	116	21	49
5	22	23	60	24	36
6	17	26	29	18	40
7	23	24	9	24	32
8	26	26	5	32	24
9	25	23	4	25	16
10	22	17	3	18	
11	20	11	3	15	
12	15	10	2	16	
13	3	13	1	4	6
14	1		1	1	0
15	1	0	0	0	0
Total	203	209	376	208	248

^a Platinum-silica-alumina catalyst. ^b Data of Egloff et al. (5).

^c Data of Greensfelder et al. (12).

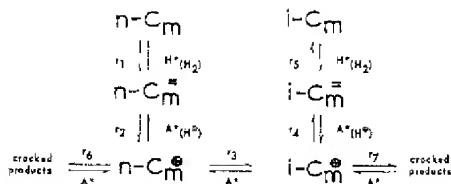


Figure 4. Relative hydrogenation activity vs. acid activity of catalyst determines whether isomers of charge will be produced in hydrocracking

C_m = cyclic with number of carbon atoms equal to m
 C^{\bullet} = olefin
 $\xrightarrow{\quad}$ = reaction rate in indicated direction, r' = reverse reaction rate; numbering corresponds to discussion in text
 \oplus = carbonium ion
 H^* = hydrogenation-dehydrogenation site reaction
 A^* = acid site reaction

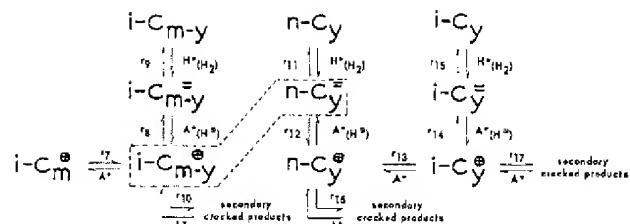


Figure 5. Charge stock is split only once (primary splitting) when hydrogenation activity is high relative to acid activity; extensive secondary splitting to low molecular weight products occurs if hydrogenation activity is low relative to acid activity

Symbols defined in Figure 4
 C_{m-y} , C_y = two fragments in splitting of C_m ; $m - y$ and y indicate number of carbon atoms
Products from splitting enclosed by dashed lines

vs. 53%), but this is still much less than with hexadecane even at lower conversions (Table IX). This increased secondary splitting of olefins at the higher conversion level in catalytic cracking is understandable if both the olefin concentrations and relative adsorptivities are considered. At low or medium conversion levels, absorption of the higher molecular weight olefin ($C_{16}^{\bullet\bullet}$) is favored over smaller olefins formed in primary splitting; thus, very little secondary splitting occurs. However, at high conversion levels, the concentration of hexadecene is reduced to low levels both by splitting and by saturation to form hexadecane by hydrogen transfer. Under these conditions, there will be increased adsorption and reaction of intermediate molecular weight olefins formed in primary splitting reactions, with the resultant increasing amounts of secondary splitting.

Isomerization of the Charge Stock. The hydrocracking mechanism must account for the fact that the uncracked charge stock at high conversion levels may either be not isomerized, as with the tungsten sulfide and nickel catalysts (7, 6), or very highly isomerized, as with the platinum catalyst in hydrocracking and with catalysts such as nickel, molybdena, chromia, platinum in hydroreforming. The reaction scheme presented in Figure 4 accounts for these widely different results. The reactions shown are illustrative of major types; other reactions of similar types are deleted for clarity. Broadly, this mechanism indicates that highly isomerized charge can be produced if the hydrogenation activity is high relative to acid activity. Conversely, if hydrogenation activity is low relative to acid activity, splitting can predominate and there can be fewer or even no isomers of the charge in the final product.

The reactions of one specific charge, n -hexadecane, are used for clarity and are representative. Hexadecane is dehydrogenated (r_1) to hexadecene by the hydrogenation component. The olefin is converted to a n -hexadecyl carbonium ion at an acid site by addition of a proton (r_2). This ion in turn is isomerized (r_3) and, by transfer of a proton (r_4), can be converted to an iso-olefin. This iso-olefin may be hydrogenated (r_5) to an isomer of the charge, or the n - or isohexadecyl carbonium ion may split (r_6 and r_7) to form lower molecular weight products.

The rate of dehydrogenation (r_1) will depend upon the activity of the hydrogenation component under reaction conditions. Equilibrium is attained only if r_1 is greater than r_2 ; hence, it is dependent particularly on hydrogenation activity

but also on acid activity. The actual concentration of the olefin will be quite low in view of thermodynamic restrictions at these hydrogen pressures. This olefin in turn can be isomerized rapidly in acidic systems (5, 27). This rate (involving r_3 and r_4) is faster than splitting reactions (r_6 and r_7) on acidic sites. This is indicated by the extensive formation of isohexadecenes in the product from catalytic cracking of n -hexadecene. This also suggests that both n - and isohexadecyl carbonium ions are present. Either may split (r_6 or r_7), but it is not now possible to differentiate rates, nor is it material to the general mechanism since both can lead to the same products. The mechanism presented here indicates that isohexadecane is not an intermediate, but is rather a by-product which may re-enter the system to give the same products as the original n -hexadecane.

The normal and iso-olefins and carbonium ions basically can undergo either hydrogenation (r_5 and r_8) or splitting (r_6 and r_7). When hydrogenation activity is high, the rate of r_5 can be much greater than r_6 and r_7 . Under these conditions, isomers of the charge would be expected (and were found). When hydrogenation activity is relatively low compared with acid activity, r_6 and r_7 can be much greater than r_5 , and little or no isohexadecane would be expected [and none was found with the nickel or tungsten sulfide catalysts (7, 6)].

Primary vs. Secondary Splitting. An extension of this reaction scheme (Figure 5) explains another striking difference in hydrocracking catalysts: The extensive secondary splitting with nickel and tungsten sulfide hydrogenation components vs. the very low degree of secondary splitting with a platinum hydrogenation component at high conversion levels.

The reaction scheme of Figure 5 is a continuation from Figure 4 which gives the source of hexadecyl carbonium ion. The isohexadecyl ion splits (r_7) to form two primary reaction products, shown here as an isoparaffin carbonium ion ($i-C_{m-y}^{\oplus}$) and a normal olefin ($n-C_y^{\bullet\bullet}$) where y represents the number of carbon atoms in the olefin. The carbonium ion can be converted to an olefin (r_8), which in turn can be hydrogenated (r_9) to an isoparaffin, or the carbonium ion can undergo secondary splitting (r_{10}). The normal olefin can either be hydrogenated on a hydrogenation site to a normal paraffin (r_{11}), or converted to a carbonium ion (r_{12}) on an acid site. When the latter occurs, isomerization (r_{13}) and proton abstraction (r_{14}) can lead to an iso-olefin. This iso-olefin in turn can be hydrogenated to an isoparaffin (r_{15}).

If hydrogenation activity is high, r_8 , r_{11} , and r_{15} are high, and the primary fragments from the primary splitting reaction (r_7) will be hydrogenated rapidly and their concentration reduced to low levels. Thus, with reduced amounts of primary olefins and carbonium ion fragments, the rates of secondary splitting reactions r_{10} , r_{16} , and r_{17} are minimized. Under these conditions little secondary splitting will occur. However, if the hydrogenation activity is low, splitting reactions r_{10} , r_{16} , and r_{17} will be higher, and secondary splitting can occur to a greater extent.

The concentrations of all olefins, both charge and products, must also be considered. Reactions r_1 and r_1' (Figure 4) and r_4' , r_{11}' , and r_{15}' (Figure 5) can supply a continuous source of olefins. With high hydrogenation activity, there is a ready source of olefins of all molecular weight ranges. Under such conditions, the higher molecular weight hexadecenes are adsorbed preferentially on acidic sites. The over-all hydrocracking reaction is then limited by acid site activity. By contrast, when reactions over acidic sites are more rapid and deplete the hexadecenes, the lower molecular weight olefins can undergo secondary cracking both because there are acid sites available and because olefins formed in splitting are not rapidly reduced in concentration by the hydrogenation component. Thus, low conversion levels should reduce secondary splitting such as was observed with the molybdena and cobalt molybdate catalysts.

This mechanism also predicts and explains why there can be even more secondary cracking in hydrocracking of hexadecane and even hexadecene over weakly hydrogenative catalysts (7) than in catalytic cracking of hexadecene. In hydrocracking, the weak hydrogenation components hydrogenate the hexadecene in preference to the lower molecular weight olefins. Thus, this reduces the hexadecene concentration required on acid sites for primary splitting, without a corresponding reduction of intermediate olefins which can undergo secondary splitting. In catalytic cracking where only acid sites are involved, there can be no corresponding hydrogenation of hexadecenes, and hydrogen transfer does not so seriously deplete the hexadecenes.

Relative Rate of Splitting at Specific Bonds. When hydrocracking hexadecane over platinum catalyst, the center bond is split at the fastest rate. This rate is taken as unity on a relative basis. The adjacent bonds split to acyclics at slower rates, the rates generally decreasing the further removed is the bond (Table X). The same type of preferential splitting was found with the molybdena and cobalt molybdena catalysts.

There is very little cracking at the α - or β -bonds to give methane or ethane when hydrocracking hexadecane. When hydrocracking heptane, the methane and ethane formation is

greater than with higher molecular weight paraffins. This may indicate a small amount of splitting by the hydrogenation component, which has been observed by Myers and Munns (7) with low molecular weight paraffins.

There is an interesting similarity in the rate of splitting of specific bonds in catalytic cracking of an olefin, hexadecene, and hydrocracking of hexadecane (Table X). At the same conversion level (53%), there are some bonds that split at appreciably different rates, but in both cases the rates decrease the further removed the bond is from the center. This fact gives further support to the proposed mechanism.

The relative rates of splitting are deduced from the acyclics. At a hydrocracking conversion as high as 82%, there are close to equivalent mole amounts of C_7 and C_9 and of C_8 and C_{10} . However, to a small degree, the moles of paraffin C_5 exceed C_{11} , those of C_4 exceed C_{12} , and those of C_3 exceed C_{13} . The total excess moles of C_5-C_6 over $C_{10}-C_{12}$ paraffins is only 21 moles. Since there are 16 moles of naphthenes, primarily C_9-C_{12} , the splitting of side chains from these cyclics accounts for most of the excess C_5-C_6 ; a small amount of secondary splitting accounts for the rest.

While hexadecane splits at a higher rate at the center bond, this should not be taken as necessarily indicating that center splitting is favored with all size molecules. For example, *n*-docosane splits to give large amounts of C_7 , C_8 , and C_9 paraffins and, apparently, the corresponding $C_{13}-C_{15}$ products since there is little secondary splitting. Also, with extensive cracking of pentatriacontene, there were large amounts of C_8 and C_9 . This suggests that carbonium ions that split are predominantly those with the charge at about the sixth or seventh carbon atom in the chain (representing the ion in the classical sigma form). A carbonium ion π -complex with a substituted ring of 5 to 6 carbon atoms can also account for the predominant splitting leading to C_7-C_9 paraffins.

Isomerization of Low Molecular Weight Paraffins. The iso to normal ratio of the lower molecular weight paraffin products exceeds thermodynamic levels in hydrocracking (as well as in catalytic cracking). It has been suggested (6) that in hydrocracking excess isoparaffins result because of rapid saturation of branched olefins which might otherwise isomerize toward equilibrium to give more normal paraffins. Based on this hypothesis, it would be predicted that the higher hydrogenation activity of platinum would give more highly isomerized light cracked products than nickel or tungsten sulfide.

However, the iso to normal ratio of the butanes was lower with platinum than with nickel and thus appears to contradict this earlier hypothesis. In contrast, the mechanism proposed here (Figure 5) predicts the lower iso to normal ratio in the cracked products with higher hydrogenation activity. Two alternate routes can account for this: a secondary isomerization of isoparaffins to give normal paraffins, more closely approaching thermodynamic equilibrium ($r_{15}'-r_{14}'-r_{13}'-r_{12}'-r_{11}'$); or, conversely, rapid saturation of normal olefin products (r_{11}).

The first alternate is probably a small factor. If this predominated, the iso to normal ratio should vary with conversion, which is not the case (Table III). With high hydrogenation activity, adsorption of low molecular weight olefins on acidic sites is apparently very small (even though present) because of the preferential adsorption of the higher molecular weight olefin charge. With low hydrogenation activity, the dehydrogenation reaction r_{15}' would not be expected to be appreciable because of competitive reaction r_1 on the hydrogenation sites.

The second explanation above predicts that the iso to normal ratio of products could vary inversely with hydrogenation activity. An initial product from splitting (the normal

Table X. Relative Rate of Splitting at Specific Bonds

Bond	Relative Rate		
	Cat. cracking ^a hexadecene, 53% conv.	Hydrocracking ^b Hexadecane 53% conv.	Hydrocracking ^b Hexadecane 82% conv.
θ	1.00	1.00	1.00
η	0.91	0.92	0.76
ζ	0.68	0.79	0.52
ϵ	0.42	0.75	0.45
δ	0.39	0.54	0.48
γ	0.39	0.13	0.14
β	0.08	0.04	0.03
α	...	0.04	...

^a Estimated from data of Egloff et al. (5). ^b Platinum-silica-alumina.

olefin $n\text{-C}_6$ in Figure 5) can be hydrogenated (r_{11}) or can react on an acidic site (r_{12}) leading to isomerization (r_{13}) or splitting (r_{14}).

The isomerization reaction ($r_{12}+r_{13}+r_{14}$) leads to an iso-olefin which can be hydrogenated (r_{15}) to an isoparaffin. These secondary reactions ($r_{12}+r_{13}+r_{14}$) indicate how isoparaffins can be formed, even when normal olefins are primary products in splitting. (This is similar to, but different in mechanism from, catalytic cracking where isoparaffin content is hypothesized to increase because normal olefins are readily isomerized, and the iso-olefins so formed are preferentially saturated by transfer reactions—in effect draining off the normal olefins.)

Thus, when the hydrogenation strength is increased relative to acid strength, reaction r_{11} increases (relative to isomerization reactions $r_{12}+r_{13}+r_{14}$), and the degree of isomerization in products should be lowered—which agrees with reported results with different types of catalysts. The hydrogenation activity therefore has a pronounced effect on the degree of isomerization of both the cracked products and the unconverted charge, but the directions of these effects are exactly the opposite—decreasing that of the cracked products, increasing that of the charge.

Polymerization. Catalytic cracking can give products with carbon number above that of the charge. Formation of aromatics also has been attributed in part to polymerization reactions (2). In platinum hydrocracking of hexadecane, no products with over 16 carbon atoms were detected. Even the very small amount of tetracyclic aromatic pyrene, $\text{C}_{16}\text{H}_{10}$, formed at high conversion was completely unsubstituted. Two factors may account for this: rapid hydrogenation of olefins reduces their concentration, and even if small amounts are formed, the catalyst has high selectivity for conversion of the higher molecular weight materials.

Cyclization. The amount of cyclization of paraffins is markedly related to the hydrogenation activity of hydrocracking catalysts. This is indicated by the extensive formation of cyclics over platinum, the lesser formation over molybdena and cobalt molybdena, and the small or negligible formation over nickel or tungsten sulfide hydrogenation components.

Cyclics form by a mechanism that differs from catalytic cracking. Further, the cyclics produced from hexadecane are primarily $\text{C}_8\text{-C}_{12}$ and thus involve two major reactions, cyclization and splitting. Evidence that cyclization occurs first and side chains are secondarily split from the rings (rather than a sequence of paraffin splitting followed by cyclization) includes: the very limited cyclization with a low molecular weight paraffin, heptane; and the decline in average molecular weight of

the cyclics at higher conversion levels, indicating further scission of larger side chains from the rings.

These results fit into the reaction mechanism presented. An active hydrogenation component should increase the concentration of intermediate (olefins or other) which are precursors to cyclization. Again relative reaction rates dictate the types of reactions. The mechanism presented here deals with hydrocracking, but in its broadest sense it may apply to isomerization, reforming, and other reactions over dual-function catalysts.

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